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In situ HT-ESEM study of crystallites growth within CeO_2 microspheres

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Abstract

Cerium dioxide is widely studied due to its potential interest in several applications, including heterogeneous catalysis. In this field, modifications of the crystallographic orientations and surface reactivity of CeO_2 can lead to activity loss of metal supported catalysts. *In situ* High Temperature-Environmental Scanning Electron Microscopy observations were then developed to monitor such evolution in CeO_2 spherical particles. Microspheres with 300–800 nm diameter were heat treated for 1–120 min in the 1000–1200 °C range. Subsequent image analysis led to monitor and quantify the crystallite growth during isotherm dwells. Two distinct mechanisms controlling the growth of crystallites in a single microsphere were then evidenced depending on the heating duration, *i.e.* oriented attachment then diffusion. Precise control of the aggregates inner structure (number of crystallites and density) was also achieved and described as a nanostructure map. These results pave the way to new opportunities in nanoparticle design.

Keywords: A. Sintering; Nanostructure; Crystallite; SEM; Cerium oxide

1. Introduction

Cerium dioxide, CeO_2, and derived solid solutions based on the incorporation of dopants have been widely studied in the past years due to their potential interest in several fields of application. Among them, one can cite the use of $(Ce^{IV},Ln^{III})O_{2-x}$ compounds as electrolytes in solid oxides fuel cells, due to their high oxygen ionic conductivity [1]. CeO_2 also received some attention as an additive for glasses, a stabilizer for ZrO_2, a glass polisher, and many others [2]. Nevertheless, its most important application today probably relates to heterogeneous catalysis, and more particularly supported metal systems, that are widely used in industrial processes dealing with mineral synthesis, gas conversion or depollution [3]. In this context, the need to achieve high catalytic activities implies to develop the preparation of noble metals as nanoparticles, but also to produce metal supports exhibiting high values of specific surface area. Among the dozens of oxides used as supports, CeO_2 is certainly one of the most important owing to its capacity to act as an oxygen buffer. The preparation of highly reactive CeO_2 nanomaterials was then developed through various methods [4].

In this framework, recent developments in the nanomaterial elaboration processes, such as shape controlled synthesis [5] and/or elaboration of mesocrystals [6] containing d or f elements by wet chemistry methods, have opened new routes to tailored structures and morphologies. Tuning the elaboration parameters (process temperature, concentrations…) combined with original syntheses schemes offer access to a wide variety of nanomaterial shapes including cubes, spheres, octahedra, and cylinders. Further pseudomorphic [7] and/or topotactic [8] transformation of these precursors by heat treatment then allows the formation of ceramic nanomaterials containing thousands of crystallites, which final size is the key factor to assess numerous properties [9]. However, nanostructure (i.e. assembly of morphological and/or textural characteristics, including average crystallite size and particle density) is generally reported to be drastically modified under heat treatment [10]. The conservation of CeO_2 particles' nanostructure thus appears as an important challenge when operating at high temperature, with the aim to avoid nano-ripening, that

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tends to increase the average crystallite size through growth mechanisms.

In this context, we propose in the present study an innovative method based upon the combination of *in situ* and *ex situ* environmental scanning electron microscopy (ESEM) observations that allows the direct control of the nanostructure of CeO_2 microspheres during heat treatments at high temperature (1000–1200 °C). First, the behavior of the crystallites composing the spheres was investigated in order to propose general trends for their size evolution during heat treatment. The dependence of the crystallite growth versus temperature was further evaluated to get new insights on the mechanisms involved in the nano-ripening process. Finally, the consequences of such phenomena over the density/porosity of the CeO_2 microspheres were determined through the elaboration of a nanostructure map, which mimics the well-known sintering maps [11].

2. Experimental

2.1. Synthesis of CeO_2 spherical particles

Precursors for CeO_2 spherical particles were prepared through a wet-chemistry route derived from the protocols reported in the literature by Minamidate [12] and Wang [13]. A solution obtained by dissolution of $Ce(NO_3)_3 \cdot 6H_2O$ salt (supplied by Sigma-Aldrich) in deionized water was used as a starting reagent. The final concentration of the cerium solution was fixed at about 0.01 M and determined precisely through ICP-AES measurements. Precipitation was then reached by adding urea as a complexing reagent. The obtained mixture was further aged at room temperature for 72 hrs, then the solution was heated gently at 90 °C for 4.5 hrs on a sand bath. The white precipitate obtained was finally separated by centrifugation at 4500 rpm, washed twice with deionized water then with ethanol, and finally dried overnight in an oven at 60 °C. SEM observations evidenced the formation of spherical particles in the 300–800 nm range (Fig. 1) while further XRD characterization (Bruker D8, $\lambda = 1.54184$ Å) confirmed the formation of cerium oxocarbonate $Ce_2O(CO_3)_2 \cdot nH_2O$ (see Supplementary data, Fig. S1) [14,15].

From additional TG analyses (not presented here), CeO_2 appeared to be easily obtained from oxocarbonate sample through a heat treatment at 400 °C during 2 hrs. This latter both ensured the dehydration of the precursor, the decomposition of carbonate groups into CO and CO_2 gaseous species, and the oxidization of Ce(III) into Ce(IV). For all the samples prepared, an isomorphic conversion was stated, thus allowing the spherical morphology to be preserved. On this basis, the temperature range investigated during the HT-ESEM study, typically 1000–1200 °C, always corresponded to the observation of CeO_2 spheres.

2.2. In situ and ex situ ESEM observations

In situ experiments were performed with a FEI Quanta 200 ESEM field-emission gun. $Ce_2O(CO_3)_2 \cdot nH_2O$ spherical particles were dispersed in acetone and deposited onto a Pt-Au10 thin foil. Such support was specifically selected to remain inert on the whole range of temperature investigated, and thus did not interact with the samples or influence the crystallites growth process. The sample was placed in a dedicated furnace directly implemented inside the ESEM chamber. Sample temperature was continuously measured using a homemade sample holder [16]. Isothermal *in situ* heat treatment and observations were then performed under 200 Pa air atmosphere in the 1000–1200 °C temperature range. In such conditions, and considering the data reported by Wang et al. [17] and Chueh and Haile [18], the O/Ce ratio ranged between 1.995 and 2 and is not expected to impact significantly the behavior of the samples. When the targeted temperature was reached, secondary electron mode images were recorded continuously each 15 s during all the heat treatment. The acceleration voltage of the electron beam was set to 30 kV. Using the furnace attached to the ESEM, the working distance usually ranged between 19.5–21 mm (due to the size of the furnace and of the heat shield). Fiji software [19] was finally used to quantify the number of crystallites, their average size and size of the spherical particles.

Complementary *ex situ* experiments were also performed in conventional furnaces. Indeed, only the secondary electron mode was available during the *in situ* observations, while additional information can be obtained using the BSE mode. On this basis, two different methods were developed (Fig. 2). The first one was called "single particle optimized *ex situ* method": $Ce_2O(CO_3)_2 \cdot nH_2O$ spheres were prepared, dispersed in acetone and deposited onto a Pt-Au10 thin foil. This sample was rapidly introduced in a furnace pre-heated at the required temperature and maintained at this temperature for a few minutes. SEM images on specific spherical particles were recorded in both secondary and backscattered electron modes. The sample was then heated again for a few more minutes according to the same procedure than previously described, this procedure being repeated 10–30 times depending on the temperature considered. Moreover, it is important to note that the SEM images were recorded on the same particles all during the heat treatment. Thus, it allows one to follow continuously the morphological changes occurring on a single particle.

The second specific *ex situ* method was called "statistical optimized *ex situ* method". $Ce_2O(CO_3)_2 \cdot nH_2O$ particles were again deposited onto a Pt-Au10 thin foil. In that case, 10 to 30 foils were prepared, depending on the experimental temperature, then each foil was rapidly introduced in a furnace pre-heated at the required temperature and maintained at this temperature for a given duration. For each foil, secondary electron and backscattered electron mode images were recorded on 30 different spherical particles. By these means, the number of crystallites was determined for each particle and led to obtain statistical data on a representative population.

The number and the average size of crystallites within the spherical particles of CeO_2 were assessed through image analysis. In this purpose, both crystallites and CeO_2 particles were assumed to be perfect spheres. If this assumption is obvious for the particles, it was also validated for the crystallites through the Rietveld refinement of PXRD data (see